## Interpretation of Molecular Device Transport Calculation

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| **Keyword:** | Density-functional theory, molecular junction devices, self-interaction error, molecule energy levels |
Interpretation of Molecular Device Transport Calculation

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Abstract

The field of molecular electronics will benefit from rational design approaches based on a complete understanding of the electronic structure of molecule-based devices. However, many computational approaches that are used to study molecular-scale devices are based on methods that have deficiencies that must be understood in order for those methods to be useful to the modelling and experimental community. Density-functional theory based methods have some well-known pitfalls that limit their application to the study of electron transport in models of molecular junction devices. Some of the impacts of these deficiencies are highlighted in this work through the use of a graphene model system and a variety of simple hydrocarbon molecule. Self-interaction error in simple functionals built from the local density approximation and the generalized gradient approximation result in very large errors in predicted absolute and relative ionization potentials. This demonstrates that electron transmission spectra predicted using these functionals should be considered with caution. We also demonstrate that care must be taken with the use of finite models for electrodes.

Keywords: Density-functional theory, self-interaction error, energy level prediction, long range-corrected methods.
Introduction

The molecular junction (MJ) is a basic building block in molecular electronics that is used to study relationships between charge transport and device structure. Many platforms are used to construct MJs, all of which involve “wiring” a molecule or molecular layer to conductive contacts so that the current across or through the molecular component can be measured. A common feature of any molecular junction is the distance scale across which charge is transferred: typically in the range of small molecule lengths often 1-10 nm, but sometimes longer. While various platforms have been used to study different aspects of the impact of molecular structure on charge transport, it has become clear that each molecular junction needs to be considered as a whole system. Clearly how the molecules, the contacts, and the different components of the junction interact with each other will influence the basic parameters that determine the “rules” for charge transport and therefore determine the electronic properties of the device.

One unique platform for the fabrication of reliable and robust, large-area molecular junctions involves covalent bonding of aromatic molecular layers onto carbon substrates, with the subsequent deposition of conductive top contacts through electron beam evaporation of Cu or carbon. A particularly interesting feature of this system is the covalently bonded molecular layer, which leads to a remarkable device stability that has enabled molecular junctions to be used in real-world applications like audio distortion circuits. However, this high level of interaction with the contact perturbs system energy levels relative to their isolated values so that the entire junction must be considered as a single system in order to obtain relevant information regarding energy level alignment. Experiments aimed at in-situ characterizations have emerged, but a more complete understanding of the molecular design “rules” would benefit the field.

First principles quantum mechanical simulations have the potential to offer valuable insights into the properties of MJs, in particular the electronic structure associated with the electrodes and the intervening molecular layer that comprise the device. In MJs, chemical structure is often expected to strongly influence the conduction properties of the devices. As we recently described, modeling of MJs comes with a number of challenges, in addition to
those described above. The strong interdependence of molecular and electronic properties in MJJs necessitates accurate information about the atomic and molecular structure of these devices. This is challenging, however, because detailed structural information associated with MJJs is often not available. Furthermore, although there is a variety of tools available to model current through MJJs and these are improving over time, currently available methods have some important limitations. These limitations may be partly responsible for disagreements between the results from modeling and experimental studies.

In this paper, we discuss two important limitations associated with simulating some components of MJJs using common density-functional theory (DFT) approaches. Firstly, we discuss some of the limitations associated with the use of finite (i.e. non-periodic) representations of graphene as a prototypical material for a bulk MJ electrode composed of carbon. Secondly, we reiterate the well-known pitfalls associated with the use of DFT-based methods for the calculation of molecular energy levels, which represent only one of many relevant device parameters. These two limitations are intertwined and should be understood by those who are interested in developing insights into MJ systems using commonly available DFT tools.

Methods

The graphene unit cell was prepared from a structure of graphite available from the Crystallography Open Database. Quantum ESPRESSO was used to optimize the structure of graphene with the PW86PBE functional and the Projector Augmented Wave (PAW) method in a plane-wave/pseudopotentials approach. The spacing between graphene layers was set to 22.5 Å. The structure so-obtained was used to prepare finite graphene models based on tetracene (see Figure 2, inset). The carbon dangling bonds at the edges of the tetracene-based models were terminated with hydrogen atoms, with C-H bond lengths set to 1.07 Å.

The molecules listed in the Appendix were geometry-optimized using LDA, BLYP, PBE, TPSS, B3LYP, PBE0, BHandHLYP, M06-2X, CAM-B3LYP, and LC-ωPBE, all with 6-31+G(d,p) basis sets using the Gaussian-09 program package. The
ionization potentials were estimated as the negative of the energy of the highest occupied molecular orbital \((-\epsilon_{\text{HOMO}}})\), as per Janak’s Theorem.$^{39}$

In the discussion below we will refer to the work function, i.e. the energy required to move an electron from the highest-occupied energy state of a bulk material at 0 Kelvin to the vacuum level, and ionization potential of molecules as physically identical processes.

Our calculations do not include the effects associated with the inclusion of semi-infinite electrodes as is normally done in non-equilibrium Green’s Function-DFT based calculations of transport. Our expectation is that the pitfalls associated with the methods outlined would persist in a transport calculation.

**Results and Discussion**

I. Finite models of bulk electrode systems: Graphene

Periodic, plane wave DFT is a practical electronic structure method currently available for the simulation of bulk systems. The application of DFT in periodic systems tends to be limited to the use of semi-local functionals such as the local density approximation (LDA) and those that make use of the generalized gradient approximation (GGA functionals). This limitation is established by the fact that exact (i.e. Hartree-Fock) exchange is non-local,$^{40}$ whereas simple DFT methods approximate exchange using semi-local functionals. Therefore, efficient DFT-based methods that contain a fraction of exact exchange are limited to computational techniques implemented for non-periodic (i.e. molecular) systems. One drawback of semi-local functionals is that they cannot consistently predict accurate energy levels of bulk and molecular systems because these functionals are affected by self-interaction error.$^{41}$ This will be discussed in detail in Part II.

The importance of accurately predicting energy levels of the electrodes and the intervening molecules in MJ's is illustrated in Figure 1. Fig. 1A shows a representation of the energy levels associated with a two-state model of a molecule sandwiched between two electrodes. The molecular states are broadened upon attachment to the electrodes as a consequence of the mixing between molecular orbitals (which are discrete in the case of
isolated molecules) and electrode states. The transmission probability associated with electrons transiting the MJ device as a function of applied voltage is shown schematically in Fig. 1B. The accurate prediction of the transmission properties of molecular junctions depend on the ability of the simulation method to accurately predict the energy levels in both the molecule and the electrodes, in addition to how the applied potential drops across the device, which is often unknown (the latter is beyond the scope of the present work). The model presented in Figure 1 therefore illustrates how the shortcomings of semi-local functionals may be problematic for the prediction of MJ transmission properties.

**Figure 1.** A) Simple energy-level diagram of a molecular junction device. The shaded bars represent the continua of states associated with two conductors, with Fermi energy levels $E_{F1}$ and $E_{F2}$, respectively. States below $E_F$ are occupied and those above are unoccupied. The highest-occupied (H, shaded) and the lowest-occupied (L, open) molecular orbitals of a molecule within the molecular junction are shown as broadened states. B) A spectrum illustrating the transmission of electrons as a function of applied voltage associated with the model system shown in A. At sufficient voltage, a broadened molecular state will be found in the bias window (between the two Fermi levels), resulting in the flow of current through the molecule.

Considering graphene as a model electrode, DFT-based methods implemented in periodic, plane wave simulation programs have known limitations in their ability to accurately predict the work function of this 2-dimensional material. Barone et al. showed that semi-local functionals such as LDA, PBE (a GGA)$^{42}$, and TPSS (a meta GGA)$^{43}$ predict work functions of ca. 4.9, 4.2 and
4.1 eV, respectively,\textsuperscript{44} whereas the measured work function for graphene is 4.6 eV\textsuperscript{45}. The errors in predicted work function arise from the self-interaction error in DFT, which can be mitigated by the inclusion of HF exchange in the DFT-based simulation methods. Some periodic, plane wave DFT programs (e.g. VASP\textsuperscript{46} and Quantum Espresso\textsuperscript{47}) have recently incorporated functionals that contain HF exchange. However, calculations employing these functionals tend to be far more time-consuming than semi-local LDA and GGA calculations because of the non-locality of HF exchange. Programs that are used to simulate transmission through molecules, for example using a non-equilibrium Green’s Function approach coupled to DFT, tend to be limited to semi-local functionals.\textsuperscript{48}

Insights into the electronic structure of graphene-based MJ devices may be developed by representing the electrode material using finite models, thereby allowing for the use of functionals that are less prone to self-interaction error. The use of finite models for graphene, for example, presents other limitations. One difficulty is that edge states develop as a consequence of dangling carbon bond termination (usually done with hydrogen). These edge states are normally the highest occupied molecular orbitals (HOMOs) and therefore may not adequately represent the top of the valence band of the electrode. Perhaps a more important limitation of the finite model approach is its inability to reproduce both the continuum of states associated with a conductor and the work function of the electrode.

To illustrate the finite model approach to the calculation of the work function in a graphene electrode, we calculated the energies of monotonically increasing sizes of finite graphene models based on tetracene unit cells with hydrogen-terminated dangling bonds. The negative of the highest occupied molecular orbital energy ($-\varepsilon_{\text{HOMO}}$) corresponds to the ionization potential according to Janak’s Theorem, and is plotted against the number of tetracene units in Figure 2. The Figure demonstrates that a finite model of graphene based on repeating tetracene units can approach the work function of the bulk material to within ca. 0.4 eV, using the LC-ωPBE functional with 6-31+G(d,p) basis sets.\textsuperscript{49,50} The reasons for selecting this functional are discussed in Part II. The ionization potential (IP) approaches from above to a limiting value of ca. 5 eV, which is reached at a number of units (n) of approximately seven. With n=7, the model has 28 fused benzene rings and a chemical formula of $\text{C}_{78}\text{H}_{24}$. It may be possible to
predict an asymptotic value that is in closer agreement with the experimental work function of graphene if larger monomer units are used (e.g. pentacene, hexacene, etc.). However, the overestimation by about 0.4 eV of the work function of graphene obtained with tetracene-based models is consistent with the overestimation of the IPs of small organic molecules that are often used in MJ devices. The consistency, which is discussed in more detail in Part II, is important in the context of the prediction of accurate energy levels of the components of MJ devices.

Figure 2: Ionization potential (negative of HOMO energy) of finite models of graphene based on tetracene as a function of the number of tetracene units, N. Calculations were performed using LC-ωPBE/6-31+G(d,p). The experimental value for the work function of graphene is shown by the horizontal line. The inset show the structure for N = 7, with a parallelogram shows two unit cells of the graphene used in the present work.
The finite model for graphene described in the foregoing may suitably represent the HOMO energy level of graphene but it does not represent well other important electronic properties of graphene. For example, at the LC-ωPBE/6-31+G(d,p) level of theory, the energy difference between the HOMO and the HOMO-1 energy levels in the finite model is almost 1 eV and the energy difference between the lowest unoccupied molecular orbital (LUMO) and the HOMO (i.e. the “band gap”) in the model is almost 1.8 eV. These energy differences, which are expected to be zero in a conductor, illustrate some important deficiencies of finite models for a conductor such as graphene. Therefore, conclusions related to the interactions between molecules and electrodes in MJ devices, based on the use of such finite models for the electrodes, must be made with caution.51 (e.g. as summarized in reference 51)

II. Accuracy of Absolute and Relative Ionization Potentials Predicted by DFT

As described above, an important limitation associated with semi-local density-functionals is their inability to predict accurate molecular (or bulk) energy levels as a consequence of self-interaction error. In the context of theoretical studies of MJ devices, the accurate prediction of absolute molecular and electrode energy levels may be less important than the accurate prediction of relative molecular and electrode energy levels. However, it is well-known that the magnitude of the self-interaction error in DFT increases with molecule size and degree of delocalization.50 Therefore, the accurate prediction of relative molecular and electrode energy levels using DFT-based methods can also be problematic.

To illustrate the impact of self-interaction error on absolute and relative energy levels using DFT-based methods, we calculated IPs as \(-\epsilon_{\text{HOMO}}\) for a series of molecules, including benzene substituted with various electron-withdrawing and donating substituents, azobenzene (used in MJ devices), linear acenes as large as pentacene, and cyclic acenes including coronene and hexabenzocoronene. The Appendix contains a complete list of molecules and the IP data. The errors in the calculated IPs, relative to tabulated52 experimental IPs, are shown in Figure 3 as linear scatter plots arranged by density-functional. Also included on the scatter plots are the IPs
predicted for the graphene model based on seven tetracenes \((C_{78}H_{24})\) that were described in Part I.

![Figure 3](image)

**Figure 3.** Linear scatter plots of the error in predicted \((-\epsilon_{\text{HOMO}})\) ionization potentials, relative to experimental values, for various acenes using several density-functionals. The average error for the set of molecules is marked with a “+” and given numerically. The error in predicted ionization potential associated with the finite model for graphene \((C_{78}H_{24})\) is shown as a magenta “x”. Negative errors indicate that the calculated IP is lower than the experimental value.

The data in Fig. 3 are arranged from top-to-bottom according to increasing amounts of Hartree-Fock exchange (HFX) incorporated into the functional. LDA, with 0% HFX, predicts IPs
for the small molecule systems with errors spread over a range from about -1 to -3 eV, with an average error of almost -2 eV. These errors compare to a predicted IP for the tetracene-based graphene model that is in almost exact agreement with the work function of graphene. It is worth underscoring that LDA’s inconsistent performance in predicting IPs points to error cancellation as the reason for its good performance for graphene. The GGA functionals - BLYP, PBE, and TPSS - also have 0% HFX, and produce similar spreads in IP errors but with average errors near -2.6 eV. Like LDA, GGAs predict IP errors for the graphene model that are much smaller than those obtained for the molecules. This demonstrates the central weakness associated with LDA and GGA functionals when applied to MJ systems: These functionals are not able to provide a quantitative or, perhaps, even a qualitative picture of the transmission spectra associated with MJ devices.

The inclusion of a small amount of HFX, as in the hybrid-GGA B3LYP (HFX=20%) and PBE0 (HFX=25%) functionals somewhat improves the predicted IPs somewhat, both in absolute and in relative terms. The spread in IP errors for the molecules decrease to ca. 1.0 eV, respectively, and the average error drops by similar amounts relative to values obtained using the corresponding GGA functionals. Inclusion of higher percentages of HFX, either directly via hybrid GGA functionals (viz. BHandHLYP, HFX=50%) or by a parameterized functional like M06-2X (HFX=56%) result in further improvements in relative IPs (spreads in error of 0.6 and 0.8 eV, respectively) and in average errors IPS (-1 and -0.7 eV, respectively).

Long-range corrected functionals, such as CAM-B3LYP (HFX(long-range)=65%/HFX(short-range)=35%) and LC-ωPBE (HFX(long-range)=100%/HFX(short-range)=0%), are known to accurately predict interactions in formal charge transfer complexes, and in noncovalently bonded complexes in which charge transfer plays some role. It follows that long-range corrected functionals should perform well for IPs and this is found to be the case in the present work. Both CAM-B3LYP and LC-ωPBE are the best performing functionals of the set applied, giving the smallest spread in errors (0.6 and 0.5 eV, respectively) and the lowest average errors (-0.6 and +0.5 eV, respectively).
The use of density functionals that minimize self-interaction error are a necessary (but
not always sufficient) condition for predicting accurate IPs.\textsuperscript{56} This fact is made clear by
inspecting the foregoing results obtained using the functionals based on Becke exchange and
LYP correlation in Table 1. The average errors in predicted IP correlate almost perfectly
\((R^2=0.989)\) with the amount of HF incorporated into the functional\textsuperscript{57} and similar results are
obtained using functionals based on PBE exchange and correlation.

**Table 1.** Error range and average errors (eV) in ionization potentials predicted using functionals
based on Becke88 exchange and LYP correlation, as a percentage Hartree-Fock exchange
incorporated in the density-functional.

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<th>%HF</th>
<th>IP Error Range</th>
<th>IP Ave. Error</th>
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<td>BLYP</td>
<td>0</td>
<td>1.49</td>
<td>2.85</td>
</tr>
<tr>
<td>B3LYP</td>
<td>20</td>
<td>1.0</td>
<td>1.96</td>
</tr>
<tr>
<td>BHandHLYP</td>
<td>50</td>
<td>0.56</td>
<td>1.05</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>65(LR)/19(SR)\textsuperscript{a}</td>
<td>0.57</td>
<td>0.66</td>
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</table>

\textsuperscript{a}LR = long-range, SR = short-range.

**Summary**

Computational simulation has the potential to provide valuable insights into the
properties and behaviour of molecular junction systems. However, the limitations associated
with presently available simulation tools must be carefully considered when assessing results
from modeling, in particular those associated with current transport. The main limitation of
current transport simulation programs is that they use LDA or GGA (semilocal) functionals in
order to obtain the electronic structure of molecular devices. We showed in the present work,
for a small set of molecular species and a single model for an electrode, that semilocal
functionals cannot predict accurate absolute and relative orbital energies of molecules that play
a key role in molecular junction systems. The impact of this shortcoming is that calculated
transmission spectra predicted for molecular junction devices will not be quantitatively correct,
and may not be even qualitatively resemble the properties of the real system under study (see
also Fig. 4 below). The development of a true understanding of the properties associated with complex, real MJ devices, requires that the simulations methods applied to them are able to systematically predict the properties of subsets of the devices with fidelity.

As a summary illustration of the differences that might be expected in transmission spectra that are predicted by semi-local functionals and LC-ωPBE, in Figure 4 we plot the

![Graph showing orbital energies](image)

**Figure 4.** Orbital energies of azobenzene on the tetracene-based model of graphene (C\(_{78}H_{24}\)), calculated using LDA (middle), BLYP (upper) and LC-ωPBE (lower), with orbitals based primarily on the model for graphene indicated by (■), (●) and (▲), for the three DFT methods, respectively. The energies of the 22 highest-lying occupied orbitals are show, with the left-most points represent the highest-occupied molecular orbital. States that are primarily based on the molecule are indicated by * and those that are centered on both the molecule and the graphene model are represented by X.
energies of the occupied orbitals for azobenzene bound to the edge of the tetracene-based graphene model, indicated as graphene, molecule, or mixed states. On the basis of Fig. 4, one might expect LDA and BLYP to produce very similar transmission spectra: The first transmission peak would occur at about 2.5 eV below the Fermi level of the graphene electrode. This peak would correspond to the relative energy between the highest energy graphene model-centered orbital and the highest energy orbital with density on both the molecule and graphene (marked by an “X” in Fig. 4). LC-ωPBE, which produces relative IPs in better agreement with the experimental values than LDA and BLYP, gives orbital energies that suggest that the first peak in the transmission spectrum would appear at ca. 4.5 eV below the Fermi level of the graphene electrode. If the LC-ωPBE results are to be believed, they suggest very different device characteristics than those suggested by LDA and GGA, namely the requirement of much higher applied voltages in order to achieve a particular degree of transport within the device.

It is worth reiterating that, while results obtained using LC-ωPBE were found to be in better agreement with experiment for the small number of molecules studied in this work, all functionals can be expected to have some shortcomings. It is important to be critical of the limitations associated with computational methodologies, and to present those limitations accordingly.18

While the present work focussed exclusively on the prediction of energy levels associated with very simple representations of two components on an MJ device, it is important to be mindful that there are many other properties that must be accurately modeled in order to provide insights into device structure-function relationships. For example, the presence, direction, and magnitude of the dipole barriers that may be present in a device can have significant impacts on device behaviour. Therefore, an energy-level only analysis of an MJ will be inherently incomplete.51

The results presented herein underscore the need for continued development of programs that predict electron transport through molecular devices. In order to be useful in the design of new devices, theoretical modeling must produce results that are in both qualitative and quantitative agreement with measured behaviour. In this connection, transport codes must
see continued development in order to incorporate advances in density-functional development.

**Acknowledgements**

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Appendix

Table A1. Calculated ionization potentials using various DFT-based methods for the molecules examined in this study. See Methods Section for the details of the calculations.

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<th>Expt(^a)</th>
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<th>TPSS</th>
<th>B3LYP</th>
<th>PBEO</th>
<th>BH&amp;HLYP</th>
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<td>C(_78)H(_24)</td>
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<td>4.58</td>
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</table>

\(^a\)Experimental, see reference 52. \(^b\)Hexabenzacoronene. \(^c\)Finite model for graphene used in the present work. \(^d\)Graphene work function as given in reference 45.
References

18. See, for example, Van Dyck, C.; Ratner, M. A.; Nano Lett. 2015, 15, 1577, which applied the Atomistix Toolkit package. 19
19. www.quantumwise.com
29. As implemented in reference 38.
46. https://www.vasp.at/
47. http://www.quantum-espresso.org/
49. Our preliminary calculations indicated that HOMO energies were essentially converged with these basis sets, which is consistent with previous work in which we showed that the electronic energy of carbon converges to the basis set limit with fairly small basis sets. See Figure S1 of reference 50.
57. The correlation was obtained using %HFX = 65 (i.e. the long-range value) for the CAM-B3LYP functional.
**Appendix**

**Table A1.** Calculated ionization potentials using various DFT-based methods for the molecules examined in this study. See Methods Section for the details of the calculations.

<table>
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<tr>
<th>Molecule</th>
<th>Expt</th>
<th>LDA</th>
<th>BLYP</th>
<th>PBE</th>
<th>TPSS</th>
<th>B3LYP</th>
<th>PBEO</th>
<th>BH&amp;HLYP</th>
<th>M06-2X</th>
<th>CAM-B3LYP</th>
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</tbody>
</table>

---

*a* Experimental, see reference Error! Bookmark not defined.  
b* Hexabenzacoronene.  
cFinite model for graphene used in the present work.  
dGraphene work function as given in reference Error! Bookmark not defined.